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Mass Estimates of Organic Compounds Buried in the Subsurface Disposal Area for Operable Units 7-08 and 7-13/14

[Prepared for: U.S. Department of Energy Idaho Operations Office Idaho Falls, Idaho]



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Page 1 of 1

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ACRONYMS

HDT historical data task

INEEL Idaho National Engineering and Environmental Laboratory

PCE tetrachloroethene

RFP Rock Flats Plant

SDA Subsurface Disposal Area

STD standard deviation

TCA 1,1,1-trichloroethane

TCE trichloroethene

VOC volatile organic compound

Mass Estimates of Organic Compounds Buried in the Subsurface Disposal Area for Operable Units 7-08 and 7-13/14

1. INTRODUCTION

1.1 Purpose

The engineering design file provides (1) updates to the mass estimates for the amounts of tetrachloroethene (PCE); 1, 1, 1-trichloroethane (TCA); and trichloroethene (TCE) found in *A Comprehensive Inventory of Radiological and Nonradiological Contaminants in Waste Buried in the Subsurface Disposal Area of the INEL RWMC During the Years 1952–1983* (LMITCO 1995), commonly known as the historical data task (HDT); (2) a determination of whether the mass estimate for methylene chloride reported in the HDT is still valid; and (3) a recommendation for further action.

1.2 Scope of Work

This work scope consists of calculations relating to the masses of PCE, TCA, and TCE in 743-series waste buried in the Subsurface Disposal Area (SDA) at the Idaho National Engineering and Environmental Laboratory (INEEL). Also included in the work scope is a short investigation to determine whether the mass of methylene chloride reported in the HDT is still valid. Methylene chloride, while not reported as a significant component of 743-series waste, is a potentially important contaminant from a risk perspective (Becker et al. 1998).

2. MASS ESTIMATES OF TETRACHLOROETHENE, TRICHLOROETHENE, AND 1,1,1-TRICHLOROETHANE

The majority of volatile organic compounds (VOCs) buried in the SDA originated from 743-series waste drums shipped to the INEEL from the Rocky Flats Plant (RFP). The RFP, which was later renamed the Rocky Flats Environmental Technology Site and subsequently renamed the Rocky Flats Closure Project, its current name, is a DOE-owned facility located 16 mi. northwest of Denver, Colorado. Because of the relatively large amount of additional process knowledge collected over the last few years about 743-series waste, it was necessary to derive updated estimates for PCE, TCA, TCE, and carbon tetrachloride (CCl₄) (estimated by Miller and Varvel [2001]) buried in the SDA. These estimates are based only on the amount of 743-series waste drums buried in the SDA.

The masses of PCE, TCA, and TCE disposed of in 743-series waste drums from RFP were calculated based on the assumption that, aside from CCl₄, the primary constituents of other VOCs included in the 743-series waste drums comprise PCE, TCA, and TCE. The remainder of this section shows how mass estimates for these chemicals were derived.

Values for total VOCs and CCl₄ masses in the 743-series waste were obtained from Miller and Varvel (2001) and used to determine the value for the volume of other VOCs, as follows:

$$OVOC = \frac{TVOC - CCl_4}{\rho_{blk}} \tag{1}$$

where

OVOC = Total volume of VOCs, other than CCl₄, in 743-series waste drums buried at the INEEL

TVOC = Total mass of VOCs in 743-series waste drums (2.4 E+06 lb standard deviation (STD) 4.5 E+05 lb)

CCl₄ = Mass of CCl₄ in the total mass of VOCs in the 743-series waste drums (1.73 E+06 lb STD 3.1 E+05 lb)

 ρ_{blk} = The assumed mean bulk density of solvents included in the 743-series waste drums

where

 $\rho_{blk} = 12.4 \text{ lb/gal}$.

Explanation: This parameter was determined by taking the midpoint of the upper and lower bounds for densities of all known VOC constituents considered to make up a significant majority of VOCs contained within 743-series waste drums. The bounds of the densities for the constituents used in the calculation were 11.2 lb/gal (TCA) and 13.5 lb/gal (PCE). The midpoint of these values is 12.4 lb/gal. The standard deviation was determined by assuming that the data follow a standard normal distribution and that the mean value is represented by the midpoint of the range. Making these assumptions, and using the "z" value at the 99.95% confidence level, the standard deviation was calculated to be 0.3 lb/gal.

Substituting the above values into Equation (1) yields the following:

$$OVOC = \frac{2.33E + 6lb - 1.73E + 6lb}{12.4lb / gal}$$

$$OVOC = 4.84E + 4gal \quad . \tag{2}$$

The standard deviation for OVOC was determined through the following equation:

$$STDOVOC = \sqrt{\frac{\left(VarTVOC + VarCCl_4\right)}{\left(TVOC - CCl_4\right)^2} + \frac{\left(Var\rho_{blk}\right)}{\left(\rho_{blk}\right)^2}} \frac{\left(TVOC - CCl_4\right)^2}{\left(\rho_{blk}\right)^2}$$
(3)

where

VarTVOC = Variance of TVOC, which is 2.0 E+011

Var CCl₄ = Variance of CCl₄, which is 9.6 E+010

 $Var\rho_{blk}$ = Variance of ρ_{blk} , which is 9.0 E-2.

Substituting the above values into Equation (3) yields the following:

$$STDOVOC = \sqrt{\frac{(2.0E + 11 + 9.6E + 10)}{(2.4E + 6 - 1.8E + 6)^2} + \frac{(9.0E - 2)}{(12.4)^2}} \frac{(2.4E + 6 - 1.8E + 6)^2}{(12.4)^2}$$

$$STDOVOC = \sqrt{1.9E + 9}$$

$$STDOVOC = 4.4E + 4gal (4)$$

Thus, the volume of VOCs, other than CCl₄, included in 743-series waste drums shipped to the INEEL for burial is 4.8 E+04 gal STD 4.4 E+04 gal.

Several mathematical methods were used in this investigation to estimate the volumetric percentages of PCE, TCA, and TCE. Results of these mathematical methods provided similar numbers but varying error. Methods using soil-gas data and groundwater data were also attempted, but the error involved with these results exceeded the general method used below. Another problem associated with using soil-gas data and groundwater data is that it is based on the current condition of waste buried in the SDA and not on waste originally disposed of. The method used in this section was the method that produced the least amount of error in the results.

The method used is based on the assumption that all three constituents (i.e., PCE, TCA, and TCE) were used in similar amounts. This assumption is based on process knowledge (ChemRisk 1992) which shows that during their heaviest use (i.e., prior to 1963), PCE and TCE were used in similar quantities. Because little information concerning the use of TCA was found for the time period of concern (i.e., prior to 1970), it was assumed that TCA was used in similar amounts as TCE and PCE. Thus, it is assumed in these calculations that PCE, TCE, and TCA each make up one third of the volume of VOCs, other than CCl₄, included in 743-series waste drums shipped to the INEEL for burial.

Because each constituent is assumed to make up one-third (33.33%) of the volume of OVOC, the STD was determined by making the assumption that the data follow a standard normal distribution and that the upper bound for the range of concern is 100%. Making these assumptions, and using the "z" values at the 99.98% confidence level, the standard deviation was calculated using the following equation:

$$STD = \frac{UB - x}{z} \tag{5}$$

where

STD = Standard deviation of x

x = Volumetric percentage (i.e., 33.33%) of PCE, TCE, or TCA in OVOC

z = The "z" value at the 99.98% confidence level, assuming a standard normal distribution (i.e., 3.49)

UB = The upper bound of the assumed range (i.e., 100%).

Solving for STD yields:

$$STD = \frac{\left(100.00\% - 33.33\%\right)}{\left(3.49\right)}$$

$$STD = 19.10\%$$
 (6)

Thus, PCE, TCE, and TCA each make up 33.33% STD for 19.10% of the VOCs, other than CCl₄, included in the 743-series waste drums shipped to the INEEL for burial.

Volumes and masses for PCE, TCA, and TCE were calculated based on the above volumetric percentages, the calculated amount of OVOC, and the respective densities for each constituent. The associated errors, including each best estimate, also were determined and reported.

The volume of each constituent was determined through the following equation:

$$V_{PCE,TCE,TCA} = OVOC * x (7)$$

$$V_{PCE,TCE,TCA} = 4.8E + 4 * 0.3333$$

$$V_{PCE\ TCE\ TCA} = 1.6E + 4gal \tag{8}$$

where

V_{PCE TCE TCA} = Volume of PCE, TCE, or TCA included in 743-series waste drums.

The standard deviation for V_{PCE,TCE,TCA} was determined using the following equation:

$$STDV_{PCE,TCE,TCA} = \sqrt{\frac{VarOVOC}{OVOC^2} + \frac{Varx}{x^2} * (OVOC * x)^2}$$
(9)

$$STDV_{PCE,TCE,TCA} = \sqrt{\left(\frac{1.9E + 9}{4.8E + 4^2} + \frac{0.0365}{0.3333^2}\right) * (4.8E + 4 * 0.3333)^2}$$

$$STDV_{PCE,TCE,TCA} = \sqrt{3.0E + 8}$$

$$STDV_{PCE,TCE,TCA} = 1.7E + 4gal \quad . \tag{10}$$

Thus, the volumes of PCE, TCE, and TCA included in 743-series waste drums buried at the INEEL were 1.6 E+04 gal STD 1.7 E+04 gal of each constituent.

2.1 Volatile Organic Compound Summary

A summary of values for the masses of PCE, TCA, TCE, and CCl₄ found in the 743-series waste stream is presented in Table 1. Masses were calculated using densities of 13.5 lb./gal, 12.2 lb./gal, and 11.2 lb./gal for PCE, TCE, and TCA, respectively. These data apply only to the 743-series waste that was not retrieved from the SDA (i.e., drums buried in pits 4, 5, 6, 9, and 10 of the SDA).

Table 1. Summary of the volumes, masses, and 95% upper-confidence levels for PCE, TCA, TCE, and CCl₄ in 743-series waste drums buried at the INEEL.

| Constituent | Total Volume gal (1) | Total Mass lb (kg) |
|-------------|----------------------|------------------------------------|
| PCE | 1.6 E+04 (6.1 E+04) | 2.18 E+05 (9.87 E+04) |
| TCA | 1.6 E+04 (6.1 E+04) | 1.81 E+05 (8.19 E+04) |
| TCE | 1.6 E+04 (6.1 E+04) | 1.97 E+05 (8.92 E+04) |
| CCl_4 | 1.4 E+05 (5.3 E+05) | 1.73 E+06 (7.86 E+05) ^a |

The values listed in Table 1 are assumed to be the most defensible values to date for each listed constituent. With the additional information from RFP (Miller and Varvel 2001), these values are more appropriate than those listed in the HDT, which are based on the Kudera (1987) report.

The new mass estimate for PCE is 360% of the best estimate value reported in the HDT, with the upper bound being 870% of that reported in the HDT. The new mass estimates for TCE and TCA are 89% and 74% of the best estimate values reported in the HDT, with upper bounds being 200% and 183%, respectively, of those reported in the HDT. The differences in the best estimates are not surprising given that the estimates in the HDT were based on 1974 inventory data from RFP. Process knowledge indicates that in the 1970s, PCE was replaced by TCA for many processes (ChemRisk 1992). Because of this and that respective mass estimates in the HDT were based on 1974 inventory data, the amount of each constituent (i.e., PCE, TCE, and TCA) estimated in the HDT may be representative of waste produced after 1970, but not representative of waste buried in the SDA.

3. METHYLENE CHLORIDE

An explanation for the best estimate of methylene chloride (i.e., dichloromethane) reported in the HDT was not found, and it is not known how the reported numbers were calculated. Because of this, an abbreviated investigation was conducted to determine whether the mass estimate of methylene chloride originally buried in the SDA, as reported in the HDT, is still acceptable. During the course of the investigation, the only information about possible sources of methylene chloride disposed of in the SDA was found in a report on RFP conducted for the Colorado Department of Health (ChemRisk 1992), and within the data collection section of the HDT (LMITCO 1995).

The ChemRisk (1992) report contains an RFP material-use profile sheet for methylene chloride (see Appendix A). The report shows that methylene chloride was used in laboratory sample preparation, paint strippers, and that "significant amounts" were used in RFP Building 889 for the cleanup of oralloy (i.e., uranium) processing line equipment from operations in RFP Building 881. It was determined that the building went into operation sometime between August and September of 1969. The waste profile sheet also corroborates this finding in a period-of-use timeline for methylene chloride at RFP. This would leave a very limited time during 1969 that methylene chloride from RFP could have been disposed of and not retrieved from burial in the SDA.

The HDT was used to determine the waste streams reported to have contained methylene chloride. These included waste stream numbers RFO-DOW-3H, -4H, -9H, and -12H, with 700, 750, 200, and 700 parts per million (ppm) of methylene chloride in each waste stream, respectively (it is assumed that ppm is equivalent to ppmv because three of the four waste streams contained contaminated debris rather than sludge). Because it was indicated in the ChemRisk (1992) report that methylene chloride was used at RFP starting in approximately 1969, the INEEL inventory database was used to determine how many drums from each of the referenced waste streams were buried in the SDA between January and December of 1969. December 1969 was used as the cutoff date because nearly all of the waste buried after December of that year was retrieved.

No references were found pertaining to the use and disposal of methylene chloride from other off-Site or on-Site generators in this abbreviated investigation. Therefore, all significant amounts of methylene chloride disposed of in the SDA are assumed to have come from RFP.

Based on assumptions from this investigation, the mass of methylene chloride was approximated and compared to the original best estimate for methylene chloride found in the HDT. For this comparison, RFP Building 889 was assumed to begin operation in August 1969. It was conservatively assumed that RFP Building 889 produced a similar quantity of liquid waste (all of which was assumed to be methylene chloride) per month as other operations buildings (e.g., Buildings 444, 776, 771, 881, and 883). This assumption is conservative because the now-demolished RFP Building 889 was used for decontamination activities and was not involved in uranium and plutonium processing operations (ChemRisk 1992), unlike Buildings 444, 776, 771, 881, and 883. For this comparison, it also was assumed that the drums from the referenced waste stream numbers buried at the INEEL during the time period of concern (i.e., January 1969 through December 1969) contained the respective concentrations of methylene chloride, as reported in the HDT. Based on the stated assumptions, a rough estimate was calculated for the mass of methylene chloride. This rough estimate was less than, but more than half of, the best estimate of methylene chloride reported in the HDT. Thus, it is concluded that the original estimate of methylene chloride in the HDT is conservatively reasonable and appropriate.

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a. Eric C. Miller, Idaho National Engineering and Environmental Laboratory, April 26, 2001, telephone communication with Jennifer Thompson, public communications representative for Rocky Flats Closure Project (the current name of the Rocky Flats Plant).

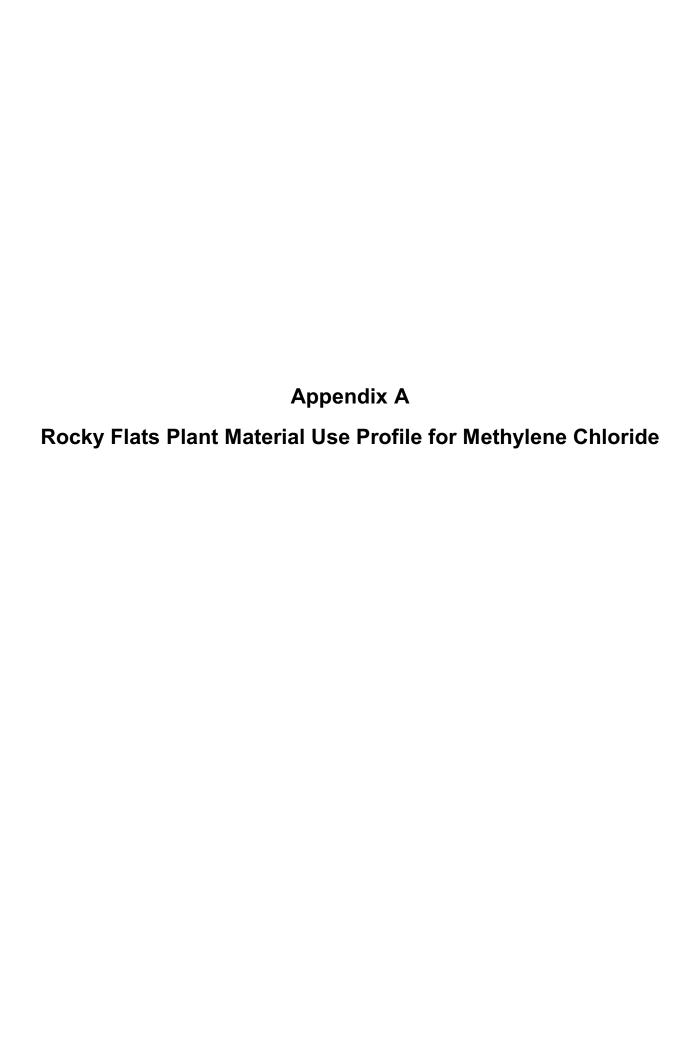
4. CONCLUSIONS AND RECOMMENDATIONS

The revised estimates for the masses of PCE, TCA, and TCE (based on the calculations in this report) changed compared to the original estimates reported in the HDT. The estimates changed because (1) additional information about waste reported to have contained CCl₄ and 743-series waste (i.e., PCE, TCA, and TCE) was found (Miller and Varvel 2001) and (2) the reported masses for PCE, TCA, and TCE in the HDT were based on an inventory report from 1974, which was not representative of waste produced and buried in the SDA prior to 1970. The mass estimates reported in this document are assumed to be more representative of waste produced at RFP and buried in the SDA prior to 1970.

Based on the abbreviated investigation into methylene chloride disposal, the amount of methylene chloride reported in the HDT is conservatively reasonable and does not need to be reestimated. This conclusion is based on finding no substantive additional information concerning methylene chloride and that methylene chloride was not reported as being disposed of in significant amounts with 743-series waste (Miller and Varvel 2001). Unless additional process knowledge is found, no further investigation should be conducted into the mass estimation of methylene chloride originally disposed of in the SDA.

5. REFERENCES

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- ChemRisk, August 1992, "Reconstruction of Historical Rocky Flats Operations & Identification of Release Points (Final Draft Report)," Colorado Department of Health, Denver, Colorado.
- Kudera, D. E., July 24, 1987, *Estimate of Rocky Flats Plant Organic Wastes Shipped to the RWMC*, Idaho National Engineering and Environmental Laboratory, EG&G Idaho, Inc., Idaho Falls, Idaho.
- LMITCO, August 1995, A Comprehensive Inventory of Radiological and Nonradiological Contaminants in Waste Buried in the Subsurface Disposal Area of the INEL RWMC During the Years 1952–1983, INEL-95/0310, Rev. 1, Idaho National Engineering and Environmental Laboratory, Lockheed Martin Idaho Technologies Company, Idaho Falls, Idaho.
- Miller, Eric C., and Mark D. Varvel, May 2001, Reconstructing the Past Disposal of 743-Series Waste in the Subsurface Disposal Area for Operable Unit 7-08, Organic Contamination in the Vadose Zone, Idaho National Engineering and Environmental Laboratory, Bechtel BWXT Idaho, LLC, Idaho Falls, Idaho.



Appendix A

Rocky Flats Plant Material Use Profile for Methylene Chloride

The document provided below was obtained from ChemRisk (1992). It describes general properties and uses of methylene chloride, as well as the specific uses of methylene chloride at the Rocky Flats Plant and the time periods when it was used.

ROCKY FLATS MATERIAL USE PROFILE;

METHYLENE CHI ODIDE

SYNONYMS: dichloromethane, DCM, methylene dichloride

CHEMICAL FORMS AND PROPERTIES:

- ! Methylene chloride is a colorless liquid with a pleasant, chloroform-like odor.
- ! Methylene chloride is moderately soluble in water and highly volatile in air.

USES BY MAN AND PRESENCE IN NATURE:

- ! Because it is an excellent solvent with low flammability, methylene chloride is used in paint removers, aerosol products, production of urethane foams and pharmaceutical products, and as a cleaning agent for metal parts and electronic components.
- ! It is also produced at low levels by chlorination of drinking water.

TOXICOLOGICAL HIGHLIGHTS:

- ! Methylene chloride is one of the least toxic chlorinated hydrocarbons.
- ! The primary route of exposure is by inhalation.
- ! Methylene chloride is a probable carcinogen (evidence in animals only).
- ! Inhalation of high levels of methylene chloride causes irritation to the eyes, nose, and throat.

USES AT ROCKY FLATS:

- ! Methylene chloride is present in paints and paint strippers used at Rocky Flats. Use was significant in Building 889, particularly in the 1960s and 1970s (e.g. clean-up of oralloy line equipment from Building 881).
- ! Methylene chloride is an ingredient of the "Cee Bee" solution used in aqueous component cleaning (EG&G, 1991f).
- ! It is used in several laboratories and process areas for sample preparation and analysis.
- ! Methylene chloride has been detected in samples of the sludge contained in the sanitary sewage treatment plant drying beds (EG&G, 1991e).

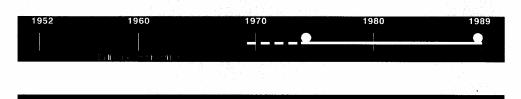
MODERN-DAY EMISSION ESTIMATE FROM EG&G APENS:

3.33 tons per year, which equals 6,660 pounds per year.

MONITORING DATA AVAILABILITY:

Methylene chloride has not been routinely monitored in airborne or waterborne effluents.

PERIOD(S) OF USE AT ROCKY FLATS:



A.1 REFERENCE

ChemRisk, August 1992, "Reconstruction of Historical Rocky Flats Operations & Identification of Release Points (Final Draft Report)," Colorado Department of Health, Denver, Colorado.